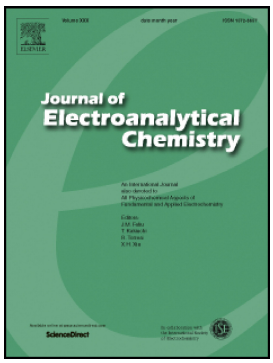

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Dynamics of Electrochemical Pt Dissolution at Atomic and Molecular Levels

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Abstract

Understanding and controlling electrochemical interfaces at atomic and molecular levels have transformed electrochemistry into a science with clearly defined fundamental principles leading to significant impact on various electrochemical systems and devices. Although the principles guiding the activity of electrochemical reactions are quite well established, the driving forces that control stability are still poorly understood. Here we utilize *in situ* monitoring of the early stages of Pt dissolution using the stationary probe rotating disk electrode technique coupled to inductively coupled plasma mass spectrometry (SPRDE-ICPMS). Our unique SPRDE-ICPMS method provides picogram sensitivity levels that, in combination with STM, provide otherwise inaccessible information about the dissolution and redeposition of Pt(111) in acidic environments. We propose two distinct dissolution mechanisms that are active during oxide formation and subsequent oxide reduction. Whereas an electrochemical dissolution mechanism is observed during anodic Pt dissolution ($Pt \rightarrow Pt^{2+} + 2e^-$), a combination of electrochemical ($PtO + 2H^+ + 2e^- \rightarrow Pt^0 + H_2O$) and chemical ($PtO^* + 2H^+ \rightarrow Pt^{2+} + H_2O$) steps control the dissolution of Pt during the cathodic scan. The redeposition of Pt ($Pt^{2+} + 2e^- \rightarrow Pt$) observed on the cathodic scan is controlled by a delicate balance between the diffusion of Pt^{2+} from the double layer and redeposition of Pt^{2+} on Pt oxide-free sites.

Keywords: Pt single-crystals; Structure-Stability relationships; Oxide formation/reduction; Dynamics of dissolution; Dissolution mechanism; Pt redeposition kinetics.

Introduction

Understanding and controlling electrochemical interfaces at atomic and molecular levels have transformed electrochemistry from primarily phenomenological event description to a